


C. Remarks

The claims are 1-11 and 14-33, with claims 1 and 31 being independent. Applicants and their attorneys acknowledge the courtesies extended to them by the Examiner during an interview with the Examiner on July 16, 2003.

The Examiner requested during the interview that the independent claims be amended to include the subject matter of claim 13. Applicants have amended claims 1 and 31 in this manner, except for the cloud temperature and boiling point boundaries, which were changed to reflect the disclosure in the specification and dependent claims 17 and 18. Also, claims 1 and 31 have been amended to specify that the oxygen-containing component comprises at least two different compounds comprising in total at least four different oxygen-containing groups and that the motor fuel is homogeneous. Support for these amendments may be found throughout the specification and, inter alia, on page 1, lines 19-22, page 17, lines 1-8, and page 78, lines 11-13. Claims 17, 18, 32 and 33 have been amended to reflect the changes in claim 1. Claims 12 and 13 have been cancelled. No new matter has been added. Reconsideration of the present claims is expressly requested.

It was pointed out during the interview that the oxygen-containing functional groups according to the presently claimed invention are alcohol ($-\text{O}-\text{H}$), ether ($-\text{O}-$), aldehyde ($-\text{C}(\text{O})-\text{H}$), ketone ($-\text{C}(\text{O})-$), ester ($-\text{C}(\text{O})-\text{O}-$), inorganic ester ($\text{O}-\text{NO}_2$),

acetal ($-\text{CH}(\text{O}-)_2$), epoxide () and peroxide ($-\text{O}-\text{O}-$) (see, e.g., page 8). These

groups can be attached singly or plurally to a single compound. In the invention, at least two (2) compounds are present in the fuel. These compounds contain at least four (4) of the above oxygen-containing functional groups. For example, the two compounds can be butylepoxystearate and ethyleneglycolmono-2-ethylhexyl ether (Example 24), which

contain four different oxygen-containing functional groups, i.e., epoxy, ester, alcohol and ether.

During the interview, the anticipation rejections over WO 95/02654 (Killick), EP 0 121 089 A2 (Majunke), EP 014 992 (Oppenlaender), GB 2,115,002A, and U.S. Patent Nos. 4,356,001; 5,405,417 (Cunningham); 4,892,562 (Bowers); 4,746,420 (Darian); 4,549,883 (Purcell); 4,522,630 (Seemuth '630); 4,536,190 (Seemuth '190); 5,766,272 (Lozzi); and 4,509,950 (Baker) were discussed.

It was pointed out to the Examiner that the goal of the present invention is to produce a motor fuel composition for diesel, gas-turbine and turbojet engines, which can both reduce the amount of deleterious pollutants and reduce the amount of petrochemicals in the fuel by substituting them with compounds that can be obtained from renewable resources. One type of additive that can be produced from renewable resources and added to fuel to reduce emission is an oxygen-containing compound. However, the addition of these compounds to, for example, diesel fuel¹ results in a number of problems. Specifically, while diesel fuel is highly non-polar, oxygen-containing compounds are polar and do not generally mix well with diesel fuel. Also, not all oxygen-containing compounds, especially compounds that are relatively less polar and more compatible with non-polar fuel, burn sufficiently well to be usable in fuel without considerably reducing engine efficiency.

With respect to miscibility, oxygen-containing compounds and diesel fuel are akin to oil and water. However, while oil and water can be combined in a form of an emulsion, an emulsified fuel is neither stable nor practical. In particular, if the fuel contains several components that do not burn sufficiently well, these components will not

¹The statements regarding fuel for diesel engines are also applicable to fuels for gas-turbine and turbojet engines.

be utilized while the other components are burned away. This can lead not only to fuel waste, but can also increase pollution and deleterious engine deposits. A homogeneous mixture avoids these problems, because burning occurs evenly throughout the mixture.

In addition, creating a polar/non-polar fuel emulsion makes the fuel highly sensitive to water, especially at extreme temperatures. Since water, which is highly polar, is difficult to eliminate upon petroleum distillation, it is invariably be present in the fuel and is attracted to the polar portion of the emulsion. Therefore, upon even a minor change in environmental conditions, the fuel tends to quickly separate, with water dissolving the polar components.

Applicants have discovered that if the oxygen-containing additives are properly selected, a polarity gradient is inherently produced. Accordingly, it is then possible to combine polar additives with the non-polar fuel to make the resulting composition homogeneous and water-tolerant. A polarity gradient in the composition can be achieved by utilizing different types of oxygen-containing functional groups. This feature is analogous to the composition of butter. Butter is formed from a plurality of different length fats of a higher to lower hydrophobicity. Despite being solid at room temperature butter spreads well due to the variety of different softening points and chain lengths of its numerous fatty constituents.

Applicants have discovered that if less than four different oxygen-containing functional groups are used, it is difficult to readily form a homogeneous, single phase fuel (page 16, lines 22-26). For example, if oleic acid, isopropyl oleate and ethanol are added to diesel oil, as disclosed in Killick, a multi-phase composition is generally observed when the mixture is permitted to stand for over an hour (page 16, lines 26-31). Only with substantial shaking does the separation disappear. Clearly, a homogeneous fuel must maintain its stability without being constantly agitated. Therefore, one of the key features of the present invention is that a fuel composition for diesel, gas-turbine and

turbojet engines should contain at least two different oxygen-containing compounds having a total of at least four different oxygen-containing functional groups, such as an alcohol, an ether, an aldehyde, a ketone, an ester, an inorganic ester, an acetal, an epoxide or a peroxide. This feature provides an appropriate gradient in polarity between the constituents so that each is substantially soluble in the next corresponding compound. More diesel-soluble components solubilize the less diesel-soluble components.

Killick discloses a fuel composition comprising ethanol, methanol, ethyl oleate and butyl benzoate (Composition 9). While these compounds have four oxygen-containing groups, these four groups are not all different from each other. Specifically, this fuel composition only has two different oxygen-containing groups: a hydroxy group and an ester group. Furthermore, this reference is silent with respect to its fuel's exhaust emissions, let alone any reduction of harmful pollutants. Also, Killick is silent with respect to the stability of the fuel. In fact, as discussed above, the fuel in Killick is not stable. Thus, Killick cannot anticipate the present invention.

Majunke is directed solely to fuel for gasoline engines, as can be clearly seen in an informal English language translation provided by Applicants during the interview, copy attached Exhibit 1. Specifically, Majunke addresses the use of bioethanol in gasolines and supergasolines. Since the present claims are related to fuel for diesel, gas-turbine and turbojet engines, Majunke clearly cannot anticipate the present claimed invention.

Sweeney is directed to a fuel composition comprising a mixture of alcohols and ethers. Alcohols and ethers, however, provide only two different oxygen-containing groups. Furthermore, this reference is silent with respect to exhaust emissions of its fuel. Accordingly, it is clear that Sweeney cannot anticipate the present invention.

Cunningham is directed to a fuel composition comprising peroxy esters and one or more organic nitrate esters. Typical organic peroxides are defined in the subject specification at page 19, lines 23-32, as compounds of the formula $R-O-O-R'$, where R and/or R' can be an oxygen-substituted alkyl, such as an alkanoic group. The specification discloses tert-butyl peroxy-acetate, which is a peroxy ester, as an example of a peroxide having one oxygen-containing functional group. The only peroxide-type compound that is considered to have two oxygen-containing groups is a hydroperoxide. Therefore, it is clear that a peroxy ester compound disclosed in Cunningham has only one oxygen-containing group, a peroxide, according to the present invention. Thus, the compounds in this reference have only three different oxygen-containing groups: a peroxide, an ether and an inorganic ester. Clearly, Cunningham cannot anticipate the present invention.

Bowers teaches that reduced emission of harmful pollutants resulting from combustion of diesel fuel can be achieved by adding a platinum compound to the fuel. The Examiner alleged that Bowers teaches a fuel composition comprising palladium acetylacetonate and an oxygenated solvent, which may be a mixture of tetrahydrofuran, methyl tertiary butyl ether and octyl nitrate. Applicants respectfully disagreed.

The platinum group metal compound in Bowers is added only in very small, catalytic amounts (col. 3, lines 12-14). The oxygen-containing compounds in the present invention are not catalysts. Therefore, to achieve the effects of the present invention, the oxygen-containing compounds must be present in more than a mere catalytic amount. Also, it should be noted that organo-metallic additives invariably result in the emission of metal oxides, which are well-known dangerous pollutants. In fact, the use of lead additives in gasoline was explicitly forbidden in the United States and many other countries for this very reason. Therefore, even though the catalytic additives disclosed in Bowers improve

burning and reduce certain noxious emissions, they create another problem by introducing poisonous metal oxides into the atmosphere.

Further, while claim 8 in Bowers states that a solvent for use with a platinum coordination compound can consist of combinations of ethanol, octyl nitrate, tetrahydrofuran and methyl tertiary butyl ether, the specification lacks any mention of a single such combination, let alone a disclosure directed to using such a combination with metal acetylacetonates. The only metal acetylacetonate is disclosed in Table 6, where palladium acetylacetonate is used with a single-component solvent: octyl nitrate. The specification in Bowers, at column 6, lines 35-41, discloses ethanol, octyl nitrate, tetrahydrofuran and methyl tertiary butyl ether as mere alternatives and does not disclose or suggest that these components are used in any combination.

Bowers teaches selecting a solvent that enhances the effectiveness of a metal catalyst (col. 6, lines 33-35). However, including an additional solvent for a metal acetylacetonate catalyst does not enhance its catalytic effect and only increases the cost of the fuel composition. In fact, a metal catalyst need not be dissolved in fuel to perform its function. It is sufficient to merely pass the fuel through, for example, a metal catalyst plate or mesh. Therefore, a skilled artisan clearly would not be motivated to select three specific solvents for a metal acetylacetonate catalyst, because using a combination of solvents increases costs without providing any disclosed benefit. The Examiner's interpretation amounts to no more than hindsight reasoning based on Applicants' disclosure, and it is clear that Bowers cannot anticipate the present invention.

Darian discloses a method for improving diesel fuel originating from off-specification diesel oils. In this method, the diesel oil is reacted with a nitrogenous treating compound and the deleterious by-products are extracted by using a solvent and a co-

solvent, which are immiscible in diesel fuel (col. 7-8). Then, the solvent and the co-solvent are separated from the fuel. The Examiner alleged that prior to separation of the solvent and the co-solvent from the diesel oil, the combination anticipates claim 1. Applicants respectfully disagreed.

The combination of the reacted diesel oil, the solvent and the co-solvent is not a stable, homogeneous motor fuel composition. Since the solvent and the co-solvent are immiscible in diesel fuel, this combination is neither stable nor a homogeneous fuel within the meaning of the present invention. In fact, the combination is not even a fuel. Darian teaches that a usable diesel fuel is obtained only after the separation (e.g., col. 8, lines 54-56). Accordingly, it is clear that this reference cannot anticipate the present invention.

Purcell teaches a fuel composition comprising a cetane improver or mixtures thereof, including 5-methyl-5-nitro-3-oxo-hexanol. The Examiner's rejection is based on the presence of the NO₂ group, the nitrate group and two ether groups.

Clearly, this is a disclosure of only two different oxygen-containing groups. The NO₂ group is not an oxygen-containing group according to the present invention and the ether groups constitute only one different oxygen-containing group. Accordingly, Purcell cannot anticipate the present invention.

Seemuth '630 discloses a mixture of alcohols and tetrahydro-2,5-furandimethanol dinitrate. However, this mixture contains at most three different oxygen-containing groups: an ether, an inorganic ester and an alcohol. Furthermore, this reference is silent with respect to exhaust emissions obtained from combustion of its fuel. Thus, clearly, Seemuth '630 cannot anticipate the present invention.

Seemuth '190 discloses a fuel composition comprising a combination of nitrates. However, such a combination provides, at most, only two different oxygen-

containing groups: and inorganic ester and an ether or an alcohol (see, e.g., col. 3, line 40 - col. 4, line 40). Furthermore, the additive in this reference, even in the form proposed for use, remains dangerously explosive and sensitive to mechanical impact. The index characterizing the explosive danger of the Seemuth '190 additives shows that these additives vary from being extremely dangerous to merely dangerous. Accordingly, it is clear that the presently claimed invention cannot be anticipated by Seemuth '190.

Lozzi discloses a fuel additive combination of dimethyl carbonate, ethylic aldehyde and ethyl nitrate. This combination, however, provides, at most, three different oxygen-containing functional groups: an aldehyde, an inorganic ester and an ester.² Therefore, Lozzi cannot anticipate the present invention.

Baker and GB 2,115,002A disclose a fuel emulsion that includes ethanol and a surfactant blend comprising poly(12-hydroxystearic acid) and polyethylene glycol. As discussed above, the present invention is directed to a homogeneous fuel composition and not an emulsion. Also, the fuel in Baker has only three different oxygen-containing groups: an ester, an ether within the polymeric chain and possibly a hydroxyl group in the chain termini. Clearly, Baker cannot anticipate the present invention.

Oppenlaender discloses a fuel composition containing, at most, a combination of polyethers, acetals, ethanol and methanol. This combination has only three different oxygen-containing groups. Accordingly, Oppenlaender cannot anticipate the present invention.


The Examiner stated during the interview that if the claims are amended to include the fuel properties recited in claim 13, the claims appear to be in allowable form, subject to further consideration and/or search.

²/The Examiner will note that a carbonate may, at most, have one oxygen-containing functional group, an organic ester, in accordance with the subject application.

Applicants have amended the claims as requested by the Examiner, with the exception of minor changes in cloud temperature and boiling point boundaries, as mentioned above. Wherefore, Applicants respectfully request favorable reconsideration of the claims, withdrawal of all outstanding rejections and expedient passage to issue of the present case.

Applicants' undersigned attorney may be reached in our New York office by telephone at (212) 218-2100. All correspondence should continue to be directed to our address given below.

Respectfully submitted,


Attorney for Applicants
Registration No. 48,512

FITZPATRICK, CELLA, HARPER & SCINTO
30 Rockefeller Plaza
New York, New York 10112-3801
Facsimile: (212) 218-2200

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Patent EP 0 121 089 B1

Description

The invention concerns motor fuel and a process to produce it consisting of a base hydrocarbon or primarily hydrocarbon fuel together with the addition of alcohols and/or ethers and/or ketones as well as additives which may be water and aromatics.

The use of methanol and ethanol as additives in conventional fuels is known. Also the addition of mixtures of methanol and tert butanol is known.

The problem of using such fuels is only partly solved so that their introduction into general use is still not possible. On the other hand the economic advantages of using alternative fuels is becoming increasingly important.

The problems consist particularly in the phase separation into alcohol and hydrocarbon phases especially at low temperatures and humid conditions, although in this case there has been some advance in the addition of methanol by simultaneously adding tert butanol as well. Butanols, being obtained from the C4 fraction of ethylene plants and only then when naphtha or medium oils are used, are not abundantly available and at relatively high cost. The use of an alternative fuel depending on a relatively high proportion of butanol is consequently rather restricted.

Other existing problems are the optimal carburetor parameters, flashpoint, density and bubble formation at high temperatures. Although the addition of pure ethanol to normal fuels in contrast to methanol leads to fewer problems, it is still not possible to use ethanol fuels in general practice which are risk free and which adhere to the *DIN Norm 51600*¹. In particular this is not possible in the case of non-absolute ethanol, which contains approximately 4.4 % by volume as a result of the formation of the ethanol water azeotrope during distillation. It is even less possible for ethanol which contains more water than that in the azeotrope at atmospheric pressure.

Economically it is of great interest to be able to mix non-absolute ethanol, especially bioethanol, with standard fuels and to have an easily available alternative fuel based on the growing domestic raw materials meeting all the demands.

The distillation of ethanol water mixtures at atmospheric pressure in a distillation column consists of 95.57 % by volume ethanol and 4.43 % by volume water at the minimum evaporation point of 78.15 deg C.

So called bioethanol is produced from natural products such as fruit, grain, potatoes, other natural, sugar containing products and also cellulose and sulphites. During processing for ethanol, which is particularly dilute, an ethanol is produced containing more water than the ethanol water azeotrope. The separation apparatus, also known as a still, can be operated continuously or in batch. Often they have at the top of the column

¹ This is the DIN norm for super gasoline [translator's note]

so called amplication columns. Depending on the design the distillation effect results in an ethanol with up to 25 % by volume water content.

Bioethanol is distilled with a rather small amount of apparatus and energy. *Since such biethanols contain organic contaminants such as aldehydes, ketones, acids and esters, their use as additives in gasoline has been considered impossible.* In addition there are problems related to mixing at environmental temperatures because of the high water content which are considered as uneconomically solvable.

A typical bioethanol for example has the following properties:

<i>Ethanol</i>	<i>78.5</i>	<i>weight %</i>
<i>Water</i>	<i>21.4</i>	<i>weight %</i>
<i>Density</i>	<i>0.8482</i>	<i>g/cm3</i>
<i>Aldehyde</i>	<i>0.10</i>	<i>weight %</i>
<i>Ketone</i>	<i>0.10</i>	<i>weight %</i>
<i>Ethylacetate</i>	<i>0.10</i>	<i>weight %</i>
<i>Acids</i>	<i>23</i>	<i>ppm</i>
<i>Condensation</i>	<i>60</i>	<i>ppm</i>
<i>Citric acid</i>	<i>2.3</i>	<i>mg/l</i>

Attempts to use pure ethanol in fuels have not lead to any particularly useful fuel because of the relatively high costs and lack of suitable distribution system. Nor is this to be expected soon. In addition there are problems with cold start, safety considerations against explosions or the problem of bubble formation at high temperatures during engine operation. Finally there is not enough ethanol in Europe.

The goal of this invention is to produce a fuel which avoids the stated problems, fulfills fuel norms, takes the suitability of additives into consideration and can be offered without restriction at gas stations.

The inventive step consists in finding a new fuel which is based on standard hydrocarbon or predominantly hydrocarbon fuel with additives of alcohols and/or ethers and/or ketones as well as aromatics, with water in addition with 0-10 % by volume ethanol – water mixture containing more water than the azeotrope, 0-10 % by volume butanol and 0-5 % by volume methanol and/or 0-15 % by volume methyl tert butyl ether and/or 0-15% by volume acetone.

After a number of laboratory and engine tests it was established that *the invented fuels are excellent for engines which can be mixed with existing fuels, fulfilling the DIN norm* and which can be offered to drivers.

The invented fuel contains 0-10% by volume ethanol with a higher water content than that found in the ethanol water azeotrope, but can also contain parts of pure ethanol and/or ethanol water azeotrope and/or ethanol or technical ethanol with less water. The preferred embodiment uses 0-5 % by volume bioethanol. Additionally, 0-5 % by volume

methanol can be used, which can be technical undistilled methanol or {abgetopptes} technical undistilled methanol. ***In the last case some of the contaminants of the methanol are removed through the head.*** Further uses according to the invention are bioethanol combined with butanols from which tert butanol is preferred, although butanol mixtures can also be used, methyl tert butyl ether and acetone. Additional mixtures can contain in certain amounts other ethers such such as dimethyl, diethyl, methyl tert amyl ether and aromatics. Also further water can be added. The acetone can be pure, technical or bioacetone.

According to claim 1 bioethanol can be combined according to the invention with

- a) butanol, methanol, methyl tert butyl ether, acetone
- b) butanols, methanol, methyl tert butylether
- c) butanols, methanol, acetone
- d) butanols, methyl tert butyl ether, acetone
- e) butanols, methyl tert butyl ether
- f) butanols, acetone
- g) butanols

The base hydrocarbon component preferably conforms with the fuels norms for super gasoline or regular gasoline or mixtures of the same. The base hydrocarbon component can contain additives which may include methanol from 0-5 % by volume and/or butanols from 0-10 % by volume whereby these are to be taken into account by the addition according to the invention of bioethanol.

Additives which can be used include a large number of such which are on the open market such as Keropur from BASF. ***Also lead in the form it is usually used in fuels can be added.***

Although the components can be mixed together such that one obtains a high octane super gasoline fuel or a lower octane regular gasoline with bioethanol, methanol, butanols, methyl tert butylether, acetone and other additives; it has nevertheless been found that the preferred method is to mix super gasoline and/or regular gasoline which may already have 0-5 % by volume of methanol and 0-10 % by volume of butanols with a premixed component, which contains bioethanol, butanols, and/or methanol and/or methyl tert butylether and/or acetone and possibly additives and lead compounds.

The results show that in this way a particularly effective and economical mixture of the components is possible and that fuel currently on the market already containing methanol and/or butanols can be used for the production of the fuels according to the invention.

The process for producing fuels according to the invention is supported by the following examples.

Example 1

A typical mixture according to the invention has for example the following formula:

50 % by volume	ethanol (78 weight %)
50 % by volume	tert butanol
0.15 g/l	lead
0.25 g/l	additive

This mixture was added to super gasoline having 3% by volume of methanol and 2 % by volume of tert butanol, where 2 % of the ethanol additive was mixed with 98 % of super gasoline.

Example 2

A mixture was produced from the following components

14.2 % by volume	ethanol (80 weight %)
42.9% by volume	methanol
42.9% by volume	tert butanol
0.15 g/l	lead
0.08 g/l	additive

This mixture was added to super gasoline having no methanol or butanol additives, where 7 % of the ethanol additive was mixed with 93 % of super gasoline.

Example 3

A mixture was produced from:

30 % by volume	ethanol (90 weight %)
30 % by volume	butanol blend (3 weight % n-butanol, 42 weight % isobutanol and 55 weight % tert butanol)
10 % by volume	acetone
30 % by volume	methanol
0.2 g/l	additive

This mixture was added to a mixture of 80 % by volume super gasoline and 10 % regular gasoline so that a mixture of 90 % by volume super / regular gasoline and 10 % by volume of oxygen containing mixture was obtained.

Example 4

A mixture was produced from:

25 % by volume	ethanol (85 weight %)
25 % by volume	tert butanol

20 % by volume	methanol
25 % by volume	methanol tert butyl ether
5 % by volume	acetone
0.25 g/l	additive

This mixture was added to super gasoline so that the mixture of 90 % by volume super gasoline and 10 % by volume of oxygen containing compounds was obtained.

Example 5

92 % by volume regular gasoline was mixed with 1.5 % by volume ethanol (80 weight %), 2.5 % by volume butanol and 4 % by volume methyl tert butyl ether.

A bioethanol super gasoline according to the invention has the following characteristics:

Density d15	0.743 g/cm ³
Octane number	
ROZ	99.4
MOZ	88.8
FOZ	93.3
Lead content	0.13 g/l
Evaporation	
At 70 deg C	41.0 % by volume
At 100 deg C	59.5 % by volume
At 180 deg C	97.0 % by volume
Upper boiling point	200 deg C
Residue	1.0 % by volume
Vapor pressure (RVP)	830 mbar
Water	2790 ppm
Methanol	3 % by volume
TBA content	3 % by volume
Ethanol (78.5 weight %)	1 % by volume
Cloud point	-20 deg C
Copper strip test	< 1
Induction time	> 720 min.
S {acid} content	< 0.001%

To a person ordinarily skilled in the art it was surprising to find that the fuels according to the invention had appreciably less carbon monoxide emissions than normal fuels. At the same time it was established that at lower and middle revolutions there was better torque with a softer engine cycle.

The experiments of the claimant have lead to a novel result in that ethanol, which contains a higher water than that of the ethanol water azeotrope at atmospheric pressure without the need for any special purification of this technical ethanol, can be added

available with the characteristics of conformance to norms, environmentally friendly, availability of the components, use in standard engines and vehicles, technically problem free production and mixing of fuels according to the invention, compatibility with existing norm conforming fuels and unrestricted mixability without danger of phase separation.

This invention is of great importance with respect to reducing the dependence on imported mineral oils as it enables for the first time the addition of bioethanol produced with relatively low energy requirements to fuels. The comprehensive tests of the claimant teach that the contaminants in this alcohol do not cause damage to the engine nor to the environment.

Claims

[See patent for claims in English.]